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J. G. Tobin, S-W. Yu, B. W. Chung, G. D. Waddill

March 3, 2010

MRS Symposium Proceedings  
San Francisco, CA, United States  
April 6, 2010 through April 9, 2010

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## Photoelectron Spectroscopy of U Oxide at LLNL

JG Tobin<sup>1,\*</sup>, S-W Yu<sup>1</sup>, BW Chung<sup>1</sup> and GD Waddill<sup>2</sup>

1. Lawrence Livermore National Laboratory, Livermore, CA, USA

2. Missouri University of Science and Technology, Rolla, MP, USA

KEYWORDS: Uranium, oxide, photoelectron spectroscopy

\*Corresponding Author: [Tobin1@LLNL.Gov](mailto:Tobin1@LLNL.Gov)

### **Abstract**

X-ray photoelectron spectroscopy has been used to characterize a sample of UO<sub>2</sub> grown on an underlying substrate of Uranium. Both AlK $\alpha$  (1487 eV) and MgK $\alpha$  (1254 eV) emission were utilized as the excitation.

### **I Introduction**

In our laboratory at LLNL, an effort is underway to investigate the underlying complexity of 5f electronic structure with spin-resolved photoelectron spectroscopy using chiral photonic excitation, i.e. Fano Spectroscopy. Our previous Fano measurements with Ce indicate the efficacy of this approach [1,2] and theoretical calculations and spectral simulations suggest that Fano Spectroscopy may resolve the controversy concerning Pu electronic structure and electron correlation. [3,4] To this end, we have constructed and commissioned a new Fano Spectrometer, [5] testing it with the relativistic 5d system Pt. [6,7] Here, our preliminary photoelectron spectra of the UO<sub>2</sub> system are presented.

Much is known about uranium dioxide, as can be found in Wikipedia. [8] “Uranium dioxide or uranium(IV) oxide (UO<sub>2</sub>), also known as urania or uranous oxide, is an oxide of uranium, and is a black, radioactive, crystalline powder that naturally occurs in the mineral uraninite. UO<sub>2</sub> is used mainly as nuclear fuel, specifically as UO<sub>2</sub> or as a mixture of UO<sub>2</sub> and PuO<sub>2</sub> (plutonium dioxide) called a mixed oxide (MOX fuel) for fuel rods in nuclear reactors. All uranium oxides were used to color glass and ceramics. Uranium oxide-based ceramics become green or black when fired in a reducing atmosphere and yellow to orange when fired with oxygen. Orange-colored Fiestaware is a well-known example of a product with a uranium-based glaze. Uranium oxide has also been used in formulations of enamel, uranium glass, and porcelain. Prior to 1960, uranium oxides were used as colored glazes.” [8]

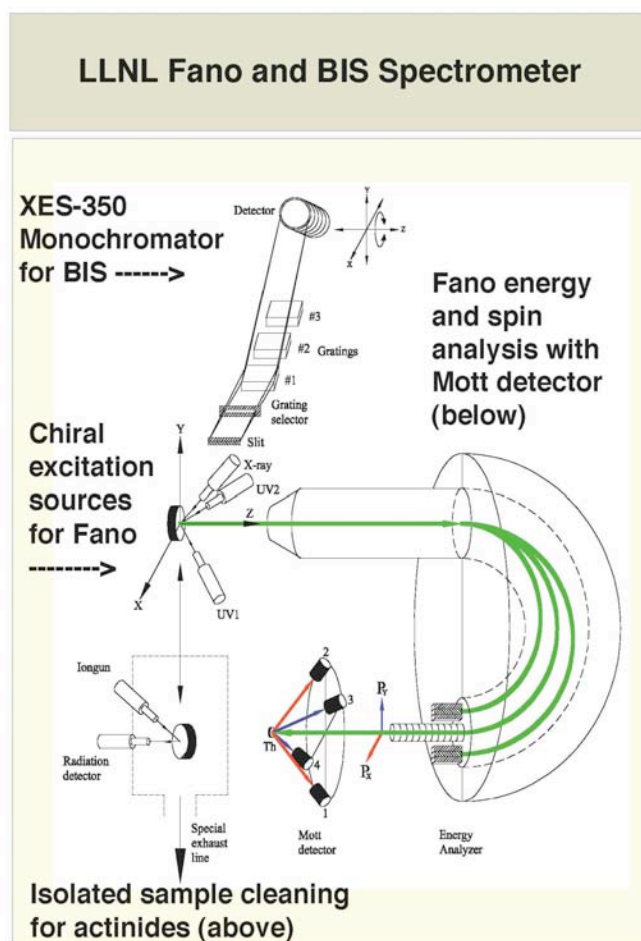
Photoelectron spectroscopy is a photon in-electron out process, with a simple relation governing the energetics:  $KE = h\nu - B_F - \phi$ . [9] Here, KE is the kinetic energy of the ejected electron.  $h\nu$  is the energy of the incoming photon.  $B_F$  is the binding energy of the electron with respect to the Fermi Level ( $E_F$ ).  $\phi$  is a work-function. In our case,  $\phi$  is a spectrometer-work-function ( $\phi_{SP}$ ) and KE is relative to that value. For our spectrometer,  $\phi_{SP} = 4$  eV, so the relations for AlK $\alpha$  and MgK $\alpha$  excitation are as follows:  $KE(AlK\alpha) = 1483$  eV -  $B_F$  and  $KE(MgK\alpha) = 1250$  -  $B_F$ .

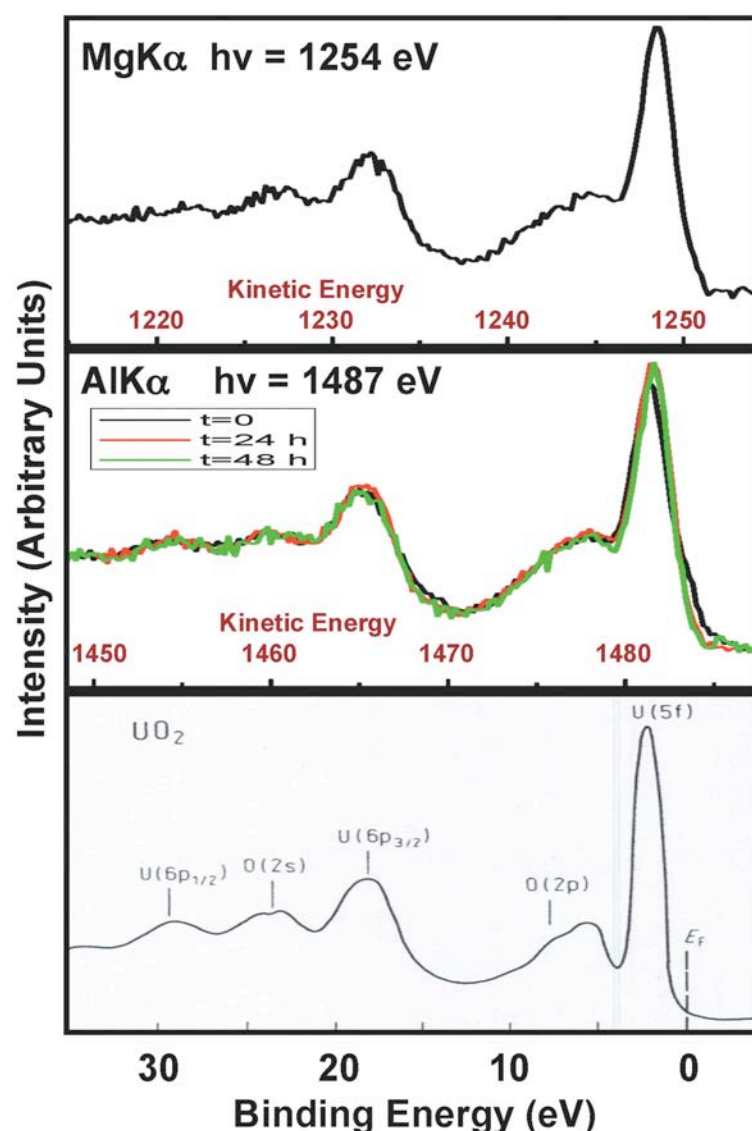
## II Experimental

The experiments were carried out onsite at Lawrence Livermore National Laboratory, using a spectrometer [5] with capabilities for performing both spin resolved Fano spectroscopy [6,7] and high energy Inverse Photoelectron Spectroscopy (IPES) or Bremsstrahlung Isochromat Spectroscopy (BIS). [10] The PES spectra were collected using a Specs x-ray source for the excitation and the Specs photoelectron energy analyzer for electron detection. The polycrystalline, depleted U sample was oxidized by exposure to air at ambient pressures. After introduction to the ultra-high vacuum system, the oxidized sample was bombarded with Ar ions and underwent annealing, to clean the topmost surface region and stabilize the surface and near surface regions. X-ray photoelectron spectroscopy (XPS) data collection occurred with the sample at or near room temperature. In our experiments, the XPS spectra play a critical role: the confirmation of the sample quality. The energy resolution band-pass in the experiment was driven by the broadening contributions of the x-ray tube and electron detection. Using the full-width at half maximum of the core level peaks, it is possible to determine directly the total energy band-pass in the XPS experiments, which is estimated to be about 2 eV. As will be discussed below, our sample consisted of a thin layer of  $\text{UO}_2$  lying above U metal. Under conditions such as these, thin layers composed of materials that would normally be insulating in the bulk can continue to exhibit a Fermi edge, owing to the thinness of the film and the underlying conductor. [11]

**Figure 1**

*Sketch for BIS and spin resolved photoelectron spectroscopy (SRPES) experimental setup installed recently at Lawrence Livermore National Lab for the electronic structure study of actinides. For BIS, the detection of the photons is performed with the XES-350 monochromator and multi-channel detector.*





*Figure 2*  
 Here is shown the comparison of the valence band spectra with an earlier result by Veal and Lam. [11] Related works can be found in the review study of Naegele. [12] The binding energy scale for all of the spectra is shown at the bottom and the respective KE scales for the AlKα and MgKα spectra are shown in their panels. Top: The MgKα spectrum. Middle: The AlKα spectrum. Bottom: The result from Veal and Lam. [11, 12]

### III Discussion

To begin, the valence band spectra will be considered. A comparison of the spectra for the LLNL sample versus the earlier work of Veal and Lam is shown in Figure 2. Both the AlKα and MgKα results are consistent with the earlier work and its assignments. There appears to be no photon-energy-dependence nor variation with time, at least over a 48 hour period. (The time independence will also be seen in the core level spectra below.) This strongly suggests that the sample is UO<sub>2</sub>, and that it is stable. There appears to be a weak Fermi edge at 0 eV ( $E_F$ ), consistent with a thin oxide layer grown on top of a metal substrate.

This assignment can be further tested by an examination of the core level and Auger spectra, accessed with the AlKα and MgKα radiation. These results will be shown in Figures 3 -7 below. Core level features are photoemission driven and are observed at a constant binding energy, while Auger peaks are generated by an electronic decay mechanism to fill core holes and are thus at fixed kinetic energies. Having both AlKα and MgKα excitation permit the separation of the two, as will be shown below. [9]

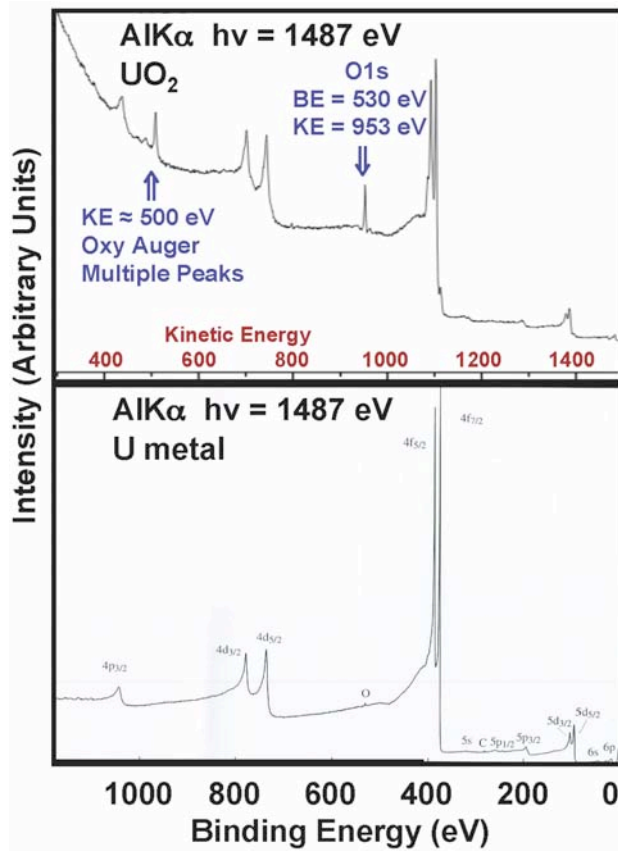


Figure 3  
 To the left.  
 A comparison our AlK $\alpha$  wide scan with that of metallic U from Reference 13. BE is binding energy. As in figure 2, the kinetic energy scale is included.

Figure 4  
 Below.  
 A comparison our MgK $\alpha$  wide scan with that of metallic U from Reference 13, following Figure 3.

Here, the comparison is made between the wide-scans of the LLNL UO<sub>2</sub> sample and the corresponding wide scans for metallic U. [13] For AlK $\alpha$  (Figure 3) and MgK $\alpha$  (Figure 4), almost all of the spectral features can be seen to be derived from the U. The exceptions are the new O1s (BE = 530 eV) and Oxygen Auger (KE near 500 eV). There are no other strong features, e.g a carbon line (C1s, BE = 280 eV). In the AlK $\alpha$  spectrum, the Oxygen Auger is isolated, but not so in the MgK $\alpha$  case.

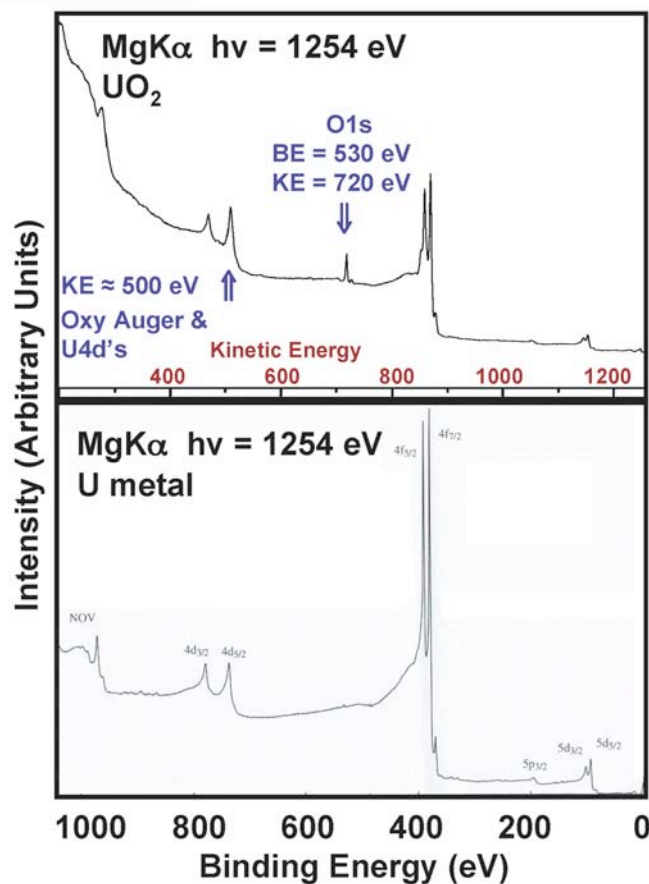




Figure 5 (below)

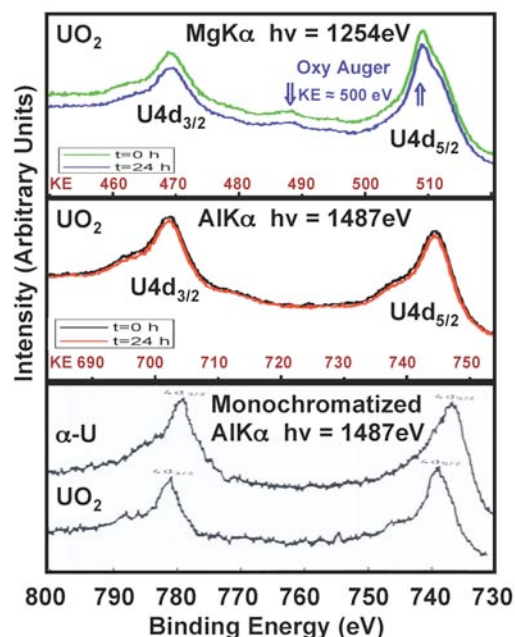


Figure 5 (caption)

The U 4d spectral region, following Figures 2-4. The reference spectra are from Ref 12 and 14.

Figure 6 (caption)

The U 4f spectral region, following Figures 2-4. . The reference spectrum is from Ref 12 and 15.

Figure 7 (caption)

The O1s spectral region, following Figures 2-4. . The reference spectrum is from Ref 12 and 15.

This overlap can be seen in Figure 5, in the MgKα spectrum. From the comparison with the reference spectra of Allen et al, the sample is UO<sub>2</sub>, not U, with the strong shoulder following each of the principal peaks.

Figure 6 (below)

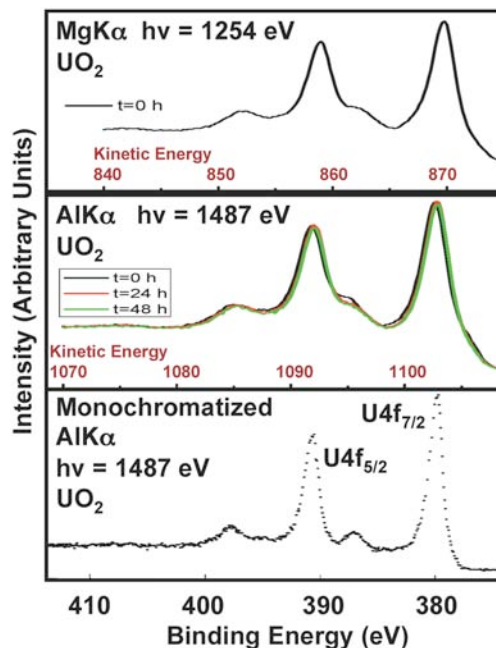
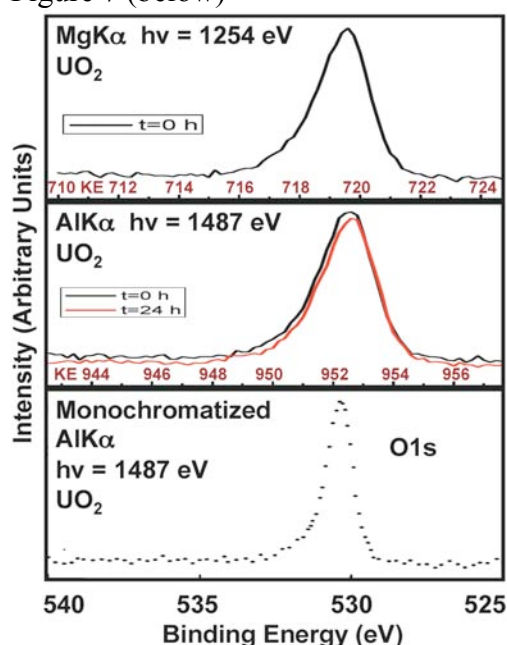


Figure 7 (below)



Similar agreement can be found in the case of the U 4f (Figure 6) spectra and O1s spectra (Figure 7). It is of particular importance that the satellite peaks are observed in the U 4f spectra. UO<sub>2</sub> has strong satellites, as shown above, but there are none for U metal. (not shown here) [12, 15, 16]

In these figures, the reference spectra were taken at substantially higher resolution. Thus, while the LLNL spectra recapture the essential features, they are broadened relative to the

reference spectra. Because the goal of this XPS study was merely to characterize the sample, higher resolution is not required. However, it does afford the chance to properly calibrate our energy band-pass. As can be seen in Figure 7, the full-width-at-half-max is about 2 eV, providing a well-grounded estimate of the band-pass.

#### **IV Summary**

Using XPS and comparing to reference spectra, it has been shown that our sample is clearly UO<sub>2</sub>.

#### **V Acknowledgments**

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award KC020202/#SCW0289.

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